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14. ABSTRACT

We achieved the synthesis, processing, properties, and morphology of polymeric nanocomposites made using highly carboxylated, soluble, ultra-short (lengths less than 60 nm) single-walled carbon nanotubes (US-SWNTs). The epoxy composite system reinforced with 0.5 wt% or 1 wt% of US-SWNTs has shown an average 15% increase in tensile modulus and 50% increase in tensile toughness over those of the neat epoxy, demonstrating the reinforcement efficacy of US-SWNTs in a thermoset matrix.

Copolymerization of short (avg. length 60 nm) carboxylic acid functionalized SWNTs with PBO oligomers was successfully carried out in a mixed solvent of polyphosphoric acid and methanesulfonic acid (MSA) in the presence of P2O5 at 3.3 wt% concentration and 150 °C. The SWNTs were homogeneously distributed throughout the films of copolymerized products.

Reaction-induced crystallization of oligomers was applied for the preparation of single-walled carbon nanotubes (SWNTs)/poly(p-oxybenzoyl) (POB) crystals using SWNTs as a nucleating agent.

The research, detailed in the publications and prior technical reports, is larger than 2 MB.

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Final Report to the Air Force Office of Scientific Research on "SWNT Composite Fibers (SCF)", for the period 4/1/2005-3/31/2008, grant number FA9550-05-1-0152

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Prior reports have provided details of the experimental research done as a result of the funding of this project. This final technical report contains a summary of the publications and patent applications that have arisen from this work.

Short, functionalized, soluble carbon nanotubes, methods of making same, and polymer composites made therefrom. Hwang, Wen-Fang; Chen, Zheyi; Tour, James M. (William Marsh Rice University, USA). PCT Int. Appl. (2008), 46pp., which. CODEN: PIXXD2 WO 2008054836 A2 20080508 Designated States W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA. Designated States RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IS, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, ML, MR, NE, SN, TD, TG. Patent written in English. Application: WO 2007-US62570 20070222. Priority: US 2006-775635 20060222; US 2006-835001 20060802. CAN 148:539453 AN 2008:556964 (Copyright (C) 2008 ACS on SciFinder (R))

Patent Family Information

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WO 2007-US62570	2008054836	A2	20080508	WO 20070222
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Priority Application

US 2006-775635P	P	20060222
US 2006-835001P	P	20060802

Abstract

In some embodiments, the present invention relates to new processes to simultaneously shorten and functionalize raw or purified carbon nanotubes to improve their dispersity and processibility, and the short functionalized nanotubes that may be made by the processes. This present invention also relates to new compns. of matter using short functionalized carbon nanotubes with thermoset, thermoplastic polymers, high temp. polymers, and other materials; the processes for making such composite materials; and the products of said processes. The process may involve exposing the carbon nanotubes to an intercalation agent (super acid) for the carbon nanotubes and with a reactive agent that is compatible and miscible with the intercalation agent. The exposure of individual carbon nanotube to the intercalation agent may render the reaction more effective in simultaneously shortening and functionalizing the carbon nanotubes so as to afford improved soly. The short functionalized nanotubes may be modified by derivatization so as to produce short functionalized nanotubes with modified functionalizing groups. The functionalizing groups may be selected for compatibility with a predetd. polymer. The short functionalized carbon nanotubes may be sol. in a variety of aprotic solvents, water, alcs., and acids. The short functionalized carbon nanotubes may disperse in other materials, for example, polymer composites and monomer blends.

Preparation of single-walled carbon nanotubes-induced poly(p-oxybenzoyl) crystals. Kobashi, Kazufumi; Lomeda, Jay; Chen, Zheyi; Azad, Samina; Hwang, Wen-Fang; Tour, James M. Department of Chemistry, Rice University, Houston, TX, USA. Journal of Polymer Science, Part A: Polymer Chemistry (2008), 46(4), 1265-1277. Publisher: John Wiley & Sons, Inc., CODEN: JPACEC ISSN: 0887-624X. Journal written in English. CAN 148:403919 AN 2008:199558 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

Crystn. of oligomers was applied for the prepn. of single-walled carbon nanotubes (SWNTs)/poly(p-oxybenzoyl) (POB) crystals using SWNTs as nucleating agent. Polymn. conditions were studied to induce the crystn. of POB oligomers through SWNTs. SWNTs/POB plate-like or lozenge-shaped crystals were successfully prepd. by direct polymn. of p-hydroxybenzoic acid (HBA) in a mixed solvent of DMF/Py with TsCl in the presence of functionalized SWNTs. The size of the plate-like crystals was ~200 nm to 3 μm. The crystals consisted of some layers, ~3 nm thick plates. Model reactions showed that esterification reactions proceed between functionalized SWNTs and HBA monomers in the polymn. system.

The obtained crystals exhibited unique morphol. and high crystallinity, producing a novel SWNT/POB hybrid composite.

Nanoscopically Flat Open-Ended Single-Walled Carbon Nanotube Substrates for Continued Growth. Kim, Myung Jong; Haroz, Erik; Wang, Yuhuang; Shan, Hongwei; Nicholas, Nolan; Kittrell, Carter; Moore, Valerie C.; Jung, Yeonwoong; Luzzi, David; Wheeler, Robert; BensonTolle, Tia; Fan, Hua; Da, Sean; Hwang, Wen-Fang; Wainerdi, T. J.; Schmidt, Howard; Hauge, Robert H.; Smalley, Richard E. Department of Physics Astronomy, Department of Chemistry and Carbon Nanotechnology Laboratory, Rice University, Houston, TX, USA. Nano Letters (2007), 7(1), 15-21. Publisher: American Chemical Society, CODEN: NALEFD ISSN: 1530-6984. Journal written in English. CAN 146:217707 AN 2006:1308072 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

Continued growth is a way of growing nanotubes targeted to produce continuous and chirality-controlled single-walled carbon nanotube (SWNT) materials. This growth method strongly depends on efficient prepn. of open-ended SWNT substrates. Nanoscopically flat open-ended SWNT substrates were prepd. by cutting the SWNT spun fiber with a focused ion beam cutting technique and followed by etching schemes for cleaning amorphous carbon and opening the ends of the SWNTs. The open ends were effectively characterized through selective etch back of open SWNT ends by carbon dioxide gas at 950 °C. High d. continued growth was demonstrated from these nanoscopically flat open-ended substrates.

Copolymer of Single-Walled Carbon Nanotubes and Poly(p-phenylene benzobisoxazole). Kobashi, Kazufumi; Chen, Zheyi; Lomeda, Jay; Rauwald, Urs; Hwang, Wen-Fang; Tour, James M. Department of Chemistry, Department of Applied Physics, Carbon Nanotechnology Laboratory, The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, TX, USA. Chemistry of Materials (2007), 19(2), 291-300. Publisher: American Chemical Society, CODEN: CMATEX ISSN: 0897-4756. Journal written in English. CAN 146:207127 AN 2006:1303118 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

The use of single-walled carbon nanotube (SWNT) copolymers in polymeric formulations may lead to better alignment of fibers, thereby producing higher performance materials. Although poly(p-phenylene benzobisoxazole) (PBO) fibers are some of the strongest org. polymer fibers known, the introduction of SWNTs into the PBO backbone might lead to improvements in their phys. properties. Therefore, copolymn. of short (av. length 60 nm) carboxylic acid functionalized SWNTs with PBO oligomers was successfully carried out in a mixed solvent of polyphosphoric acid and methanesulfonic acid (MSA) in the presence of P2O5 at 3.3 wt. % concn. and 150 C. The SWNTs were homogeneously distributed throughout the films of copolymd. products, as detd. by Raman spectroscopy using the diagnostic radial breathing mode and D and G band emissions. Morphol. differences between the copolymd. product and a phys.

mixt. were readily seen using at. force microscopy. The pptd. copolymd. nanotubes were sepd. by centrifugation from the MSA suspension of the products of short SWNTs and PBO oligomers. That benzoxazole moieties could be formed between the carboxylic acids of ultra-short (US) SWNTs and o-aminophenol derivs. was established by the condensation of US-SWNTs with o-aminophenols, and subsequent anal. of the products.

From bucky pearls to armchair quantum wires. Fan, Hua; Parra-Vasquez, A. Nicholas G.; Booker, Richard; Chen, Zheyi; Hwang, Wen-Fang; Hauge, Robert; Pasquali, Matteo; Smalley, Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, TX, USA. Abstracts of Papers, 232nd ACS National Meeting, San Francisco, CA, United States, Sept. 10-14, 2006 (2006), PRES-043. Publisher: American Chemical Society, Washington, D. C CODEN: 69IHRD Conference; Meeting Abstract; Computer Optical Disk written in English. AN 2006:865335 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

We report progress on our efforts of converting purified single wall carbon nanotubes (SWNT) into continous fibers. This process is key to the eventual development of the Armchair Quantum Wire (AQW), a continuous wire of perfectly aligned, neat, all-metallic, armchair SWNTs. The AQW will be invaluable for the next generation of aerospace applications, elec. propulsion and power distribution applications. Purified neat SWNTs in the form of bucky pearls are disentangled with a new process to prep. a starting material which is easier to mix and yields better aligned SWNTs fibers. We introduce a new process of co-extrusion of SWNTs and rigid rod polymers to further align the SWNTs in the core by drawing of a co-flowing sheath of polymer soln. This process preserves the elec. cond. of SWNTs because the SWNTs and the polymers don't intermix, at the same time, the polymeric sheath provides addnl. mech. support.

Soluble single-walled carbon nanotubes. Chen, Zheyi; Rauwald, Urs; Kobashi, Kazfumi; Hwang, Wen-Fang; Tour, James M. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, TX, USA. Abstracts of Papers, 232nd ACS National Meeting, San Francisco, CA, United States, Sept. 10-14, 2006 (2006), INOR-052. Publisher: American Chemical Society, Washington, D. C CODEN: 69IHRD Conference; Meeting Abstract; Computer Optical Disk written in English. AN 2006:860448 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

Aprotic solvent and water sol., ultra short (length < 60 nm), sidewall- and end-carboxylated, single-walled carbon nanotubes (SWNT) can be prepd. by a scalable process. This process is an improved cutting procedure using mixt. of sulfuric and nitric acids. Because super sulfuric acid (>100% H2SO4 with excess SO3) is known to intercalate SWNT ropes more effectively, the current process uses oleum (sulfuric acid with 20% excess of SO3) instead of 98% or 96% sulfuric acid used in the previous methods. This two-steps process consists of (1) intercalation of sulfuric acid mols. between individual SWNT inside the SWNT ropes (2) the introduction of nitric acid, the cutting/shortening agent, into the acid-intercalated SWNT dispersion affords an efficient, and more uniform, cutting/shortening and functionalization of SWNT. The soly. of

these SWNT in aprotic solvent such as NMP, DMF is at least an order of magnitude higher than the best of those previously reported, while their soly. in water is as least as good as the best reported.

Soluble Ultra-Short Single-Walled Carbon Nanotubes. Chen, Zheyi; Kobashi, Kazufumi; Rauwald, Urs; Booker, Richard; Fan, Hua; Hwang, Wen-Fang; Tour, James M. Smalley Institute for Nanoscale Science and Technology Carbon Nanotechnology Laboratory Department of Chemistry, Rice University, Houston, TX, USA. Journal of the American Chemical Society (2006), 128(32), 10568-10571. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 145:148295 AN 2006:729415 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

Sol., ultra-short (length < 60 nm), carboxylated, single-walled carbon nanotubes (SWNTs) have been prepd. by a scalable process. This process, predicated on oleum's (100% H2SO4 with excess SO3) ability to intercalate between individual SWNTs inside SWNT ropes, is a procedure that simultaneously cuts and functionalizes SWNTs using a mixt. of sulfuric and nitric acids. The soly. of these ultra-short SWNTs (US-SWNTs) in org. solvents, superacid and water is about 2 wt%. The availability of sol. US-SWNTs could open opportunities for forming high performance composites, blends, and copolymers without inhibiting their processibility.

Electron spin resonance on carbon nanofibers. Chipara, Mircea; Hauge, Robert H.; Fan, Hua; Booker, Richard; Peng, Haiqing; Hwang, Wen Fang; Zaleski, J. M.; Smalley, Richard. Indiana University, Bloomington, IN, USA. Materials Research Society Symposium Proceedings (2006), 887(Degradation Processes in Nanostructured Materials), 41-45. Publisher: Materials Research Society, CODEN: MRSPDH ISSN: 0272-9172. Journal written in English. CAN 145:49627 AN 2006:372503 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

Crude carbon nanofibers obtained from purified single-walled carbon nanotubes were examd. by ESR spectroscopy. The angular dependence of the resonance line was studied. The preferential orientation of single-walled carbon nanotubes is confirmed by the angular dependence of the g-factor and of the resonance line width.

Continued growth of single-walled carbon nanotubes. Wang, Yuhuang; Kim, Myung Jong; Shan, Hongwei; Kittrell, Carter; Fan, Hua; Ericson, Lars M.; Hwang, Wen-Fang; Arepalli, Sivaram; Hauge, Robert H.; Smalley, Richard E. Center for Nanoscale Science and Technology, Carbon Nanotechnology Laboratory, Department of Chemistry and Department of Physics, Rice University, Houston, TX, USA. Nano Letters (2005), 5(6), 997-1002. Publisher: American Chemical Society, CODEN: NALEFD ISSN: 1530-6984. Journal written in English. CAN 142:439292 AN 2005:122923 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

The authors demonstrate the continued growth of single-walled carbon nanotubes (SWNTs) from ordered arrays of open-ended SWNTs in a way analogous to epitaxy. Nanometer-sized metal catalysts were docked to the SWNT open ends and subsequently activated to restart growth. SWNTs thus grown inherit the diams. and chirality from the seeded SWNTs, as indicated by the closely matched frequencies of Raman radial breathing modes before and after the growth.